

STRUCTURAL CHARACTERISTICS OF VITRINITES

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INTRODUCTION

It is generally accepted that the various petrographic constituents of coals are derived largely from partly decayed organs of the higher plants and the chemical substances in them. Lignin, in particular, is thought to be an important part of the input to coalification processes both in preserved woody tissue and after the microbial action. The nature of the substances from which coals are derived are fairly well known. However, the chemical structures that they give rise to in coals are poorly understood. It was thought worthwhile to undertake a structural study of a set of vitrinite-rich coals (ie, derived from woody tissue), using experimental approaches that would assist in evaluating the extent to which lignin structures are still recognizable after coalification. A reductive degradation method of Burges et al (1), which has previously revealed the presence of lignin-derived phenols in the humic acids of soils, was adopted. Since coals of higher rank than lignites do not contain humic acids, humic-acid-like materials were generated in high yields (80 - 110 percent) by a mild oxidation (2) using aqueous performic acid and the products subjected to the reductive degradation.

Paleobotanic studies show that the main types of plants that contributed to coal formation in the Carboniferous were primitive gymnosperm, tree ferns, seed ferns and club mosses. In the other main eras of coal formation, the Cretaceous and the Tertiary, the source plants were angiosperms of the modern type. It is observed that there is likely to be a significant spread in some structural features of the lignin and flavonoids in such a wide range of plant types. Therefore, geological history is also considered a potentially important factor in determining structural characteristics of vitrinites. Two peat samples, three lignites and thirty-eight subbituminous and bituminous coals were studied. The mixtures of phenols and phenolic acids obtained as trimethylsilyl ethers and esters were analyzed by gas chromatography/mass spectrometry.

EXPERIMENTAL INVESTIGATION

Selection of Coal Samples

For this study three sets of coals from different geological provinces were selected. These coals are rich in vitrinite plus pseudo-vitrinite (70 - 90 percent), and cover a wide range of rank. Ten coals each from Eastern and Interior provinces and fifteen coals from Rocky Mountain province were selected. Three lignites were selected from Texas and North Dakota. Two peat

samples were taken from the Southern Everglades of Florida. Details on the analysis of selected peat, lignitic, subbituminous and bituminous coal samples are given in Reference (3).

Experimental Method

The oxidation of coal by performic acid was carried out under controlled conditions and the temperature was maintained at 50 - 55°C. Humic acids were extracted from peats and lignites with 0.5 N NaOH and from oxidized coals with 1 N NaOH. The washed and dried humic acids were dissolved in NaOH, treated with 3 percent freshly prepared sodium amalgam, and the solution was heated in an oil bath to temperatures of 110 - 115°C for 4 - 5 hours. The resulting phenols and phenolic acids were precipitated and extracted by centrifugation with ether and methylene chloride. The solvents were removed and the residues were treated with sylo HTP reagent under the specified conditions for converting phenols and phenolic carboxylic acids to their corresponding ethers and esters. The trimethyl ethers and esters were analyzed by gas chromatography with and without coinjection. A few of the identifications were made by Bimer et al (4) by gas chromatography with coinjection of standards. With the wider range of coals and with a wider set of standards more compounds were identified using GC/MS/Computer System. Experiments showed OV 101 Column Packing (3 percent on 80/100 mesh supelco port) to be the most effective for GC and GC/MS of the six packings tested. The GC/MS instrument was provided with a data system. The data system was used to subtract the mass spectrum at the foot of each peak just before it began to elute, or just after the elution, from the spectrum recorded as the maximum of the peak was eluted. The raw MS data, described above, were reported for standards and unknowns as printouts tabulating m/e values and relative intensities. The comparisons were made by visual inspection of the printed data and the retention times.

EXPERIMENTAL RESULTS

It is impracticable to reproduce here all the chromatograms and all the mass spectra obtained. Most of them are illustrated in Reference (3). It is observed that humic acids obtained both by the extractions of lignites and the oxidation of the insoluble residues, and the humic acids obtained from most (but not all) of the coals from the Rocky Mountain Province, gave poorly resolved chromatograms, while those from the Carboniferous coals of Interior and Eastern Provinces gave chromatograms where resolution ranged from reasonable to excellent. The products from the peat humic acids showed moderately good resolution. Taking an overview, 18 of 43 samples studied showed poor resolution.

There are a number of difficulties in discussing the compounds identified and assessing their significance. Humic acids are poorly defined substances of diverse origin, and their structures are unknown. In order to facilitate discussion of the distribution of compounds identified, all of the compounds partially or completely identified are listed in Table 1-3, where the coals from which they come are classified partly by rank and partly by the province. In each set of tables, the compounds are listed as far as possible in order of increasing complexity.

In Table 1 are presented the phenols and acids whose structures are simple or nonspecific about their origin. Table 2a contains compounds that appear to have been derived from the A ring of flavonoids. In Table 2b are compounds of more complex structure with a very clear relationship to the breakdown products of lignin and B ring of flavonoids. Table 3 lists relatively complex compounds which again may have had a biological origin, but this cannot be proved; for many of them the substitution pattern in the benzene ring has not been identified. What is shown in the tables is the frequency of occurrences of the various compounds. At the head of each column of the tables is shown the total number of samples of each class studied, and against the name of each compound is shown the number of reaction products in which it was identified.

Throughout the study, a number of relatively large peaks could not be matched with the Standards available, and no more than the general character of the Structure could be inferred from the mass spectra. These peaks were scanned for negative as well as positive information. The principle conclusions arising from the examination of unidentified peaks were as follows:

1. A majority of the large unidentified peaks represented phenols or phenolic acids.
2. Some evidence of the presence of biphenyl groups was seen.
3. In each chromatograms presence of hydroxy pyridines is seen.
4. No evidence of the presence of Sulfur compounds was seen.
5. Some mass spectra indicate the presence of either linkages (other than methoxyl) and of Carbonyl compounds.

DISCUSSION OF RESULTS

The most striking result of the whole study is the presence of cinnamic acid, which was found in 42 out of the 43 materials analyzed; the one product that did not contain cinnamic acid did contain the corresponding alcohol. The acid is found in a region of the chromatograms where the peaks rise directly from the baseline in almost all cases, and the peak corresponding to it was almost always sharp and intense. In addition, substances closely related to it were found in a few products, with the aliphatic side chain in a different state of oxidation, ie, not as $-\text{CH}=\text{CH}-\text{COOH}$ but as $-\text{CH}_2\cdot\text{CO}\cdot\text{COOH}$ or $-\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ or $-\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$. However, cinnamic acid is of common occurrence in plants as a biosynthetic precursor to lignin, flavonoids and phenylalanine, so that it could have entered peats as such and be incorporated into peat humic acids.

There is also present in many samples a group of compounds related to p. hydroxycinnamic acid (or p. coumaric acid). Again the side chain is in various states of oxidation ($-\text{CH}=\text{CH}-\text{CH}_2\cdot\text{OH}$, $-\text{CH}_2\cdot\text{CO}\cdot\text{COOH}$, $-\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$). p. Coumaric acid itself is the most abundant of these, being found in about

half the products from subbituminous and bituminous coals, but only in one of the lower rank materials. On the other hand, p. hydroxybenzoic acid, which can be derived from coumaric acid and related compounds by oxidation of the side chain, was found in almost all of the low rank materials and in rather less than half of the products from the higher rank coals.

There are a large group of compounds related to 3-methoxy-4-hydroxycinnamic acid (ferulic acid). This substitution pattern is the most abundant in the lignin of Gymnosperms and in some less highly evolved plants such as the Lycopods, but is found also in Angiosperms. Vanillin (3-methoxy-4-hydroxybenzaldehyde), formed in peats by microbial oxidation of ferulic acid was found in every one of the low rank materials studied, in 12 out of 15 samples from the Rocky Mountain Province, and in about one-half of those from the other provinces. In addition, the related compound, vanillic acid was found to be quite abundant. Ferulic acid itself, and caffeic acid (3,5-dihydroxycinnamic acid) were each found in about 40 percent of the samples; a sample that contained one in general did not contain the other. Oddly enough, caffeic acid is the only substance in this group that has had the original 3-methoxy substituent demethylated to hydroxy. The other substances in this group contain the aliphatic side chain in various states of oxidation, of greater variety than was found with the compounds related to coumaric acid ($-\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\text{OH}$) $-\text{CH}_2\cdot\text{CO}\cdot\text{COOH}$, $-\text{CH}_2\cdot\text{CH}_2\cdot\text{CHO}$, $-\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{OH}$ and $-\text{CHOH}\cdot\text{CHOH}\cdot\text{COOH}$.

The final group of substances related to lignin have the 1, 3, 4 and 5 substitution pattern in the benzene ring. As with the groups already discussed, the side chain was found in a variety of oxidation states. Again only one demethylated derivative was found 3, 4, 5-trihydroxycinnamic acid. What might be termed the parent compound, 3, 5-dimethoxy-4-hydroxycinnamic acid, was found in 11 samples which was entirely restricted to the higher rank materials. Syringic acid and syringaldehyde, in which two of the carbon atoms in the aliphatic chain have been removed by oxidation, were the most frequently found members of this group (19 and 13 samples respectively), and their occurrences were fairly evenly distributed over all classes of coals, including the peats.

CONCLUSIONS

By no means all of the substances that gave peaks on the chromatograms were identified, but a careful scrutiny of the data showed that identifications made were reasonably certain. The products derived from the Carboniferous coals of the Interior and Eastern Provinces were markedly less complex mixtures, and the degree of resolution was considerably better. From the results there are a number of important implications for understanding the chemistry of vitrinites. These may be summarized as follows:

1. Many benzene rings in vitrinites bear not only an OH group but often one or two methoxy groups as well; occasionally a second OH group may be present instead of methoxy. This would explain, among other things, the difficulty of sulfonating or nitrating vitrinites without accompanying oxidation.

2. Methoxyl groups survive in vitrinites to a considerably higher level of rank than previously reported.
3. Bicyclic and polycyclic aromatic ring systems, other than biphenyl, appear to be less frequent. It is possible that most of the polycyclic structures from coals accumulated in the ether-insoluble material.
4. The structure of vitrinites, even of High Volatile A Bituminous rank, appears to be similar to that of lignin, in being based to an important extent on phenyl propane and phenyl methane skeletons.
5. Olefinic double bonds are abundant in vitrinite structures as such or they are generated by the degradation processes used, in a manner difficult to envisage at this time.

The conclusions are consistent with a feasible interpretation of the X-ray scattering data of Hirsch (5). Further, it is also consistent with the conclusions of Montgomery et al (6) and of Chakrabartty et al (7) on their studies of the products of severe oxidation of coals.

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TABLE 1

Simple Phenols and Acids Identified

Compound	Direct Humic Acid		Humic Acid from Oxidized Coals			
	2	3	Lignites	15 Rocky Mountain Province Coals	10 Interior Province Coals	10 Eastern Province Coals
Acetic Acid						
Propionic Acid						
Benzoic Acid	2	1	1	2	1	1
Phenol	2	3			1	1
p-Cresol	2	1	1	3	5	3
o-Methoxy Phenol	2	2	2	12	2	4
m-Methoxy Phenol	2		2	3	2	
Hydroquinone	1	1	2			
m-Hydroxy Benzoic Acid	1	1		3	1	1
Catechol	2	2		7	5	3

TABLE 2a

Phenols Identified Having Biological Associations
(A-ring of Flavonoids)

Compound	Direct Humic Acid		Humic Acid from Oxidized Coals			
	2	3	Lignites	15 Rocky Mountain Province Coals	10 Interior Province Coals	10 Eastern Province Coals
Resorcinol	2	1		7	2	3
Phloroglucinol	2			2	1	1
2-Methyl Resorcinol		1	1	3	4	5
2,4-Dihydroxy Toluene	1	3	2	7	3	5
o-Hydroxy Benzoic Acid				5	2	1
2,4,6-Trihydroxy Benzoic Acid	1	1	1	1	1	1
2,4,6-Trihydroxy Toluene					1	5

TABLE 2b

Phenols Identified Having Biological Associations
(Lignin and its Precursors; A-ring of Flavonoids)

Compound	Direct Humic Acid		Humic Acid from Oxidized Coals			
	2 Peats	3 Lignites	3 Lignites	15 Rocky Mountain Province Coals	10 Interior Province Coals	10 Eastern Province Coals
Cinnamic Acid	2	3	3	14	10	10
Cinnamic Alcohol				1		
Phenyl, 3-Pyruvic Acid	1	1			2	2
Phenyl, 3-Propionic Acid				1	1	1
Phenyl, 3-Pyruvic Alcohol				2		
p-Hydroxy Benzoic Acid	2	3	3	5	4	3
p-Coumaric Acid			1	6	4	5
p-Coumaryl Alcohol	1			1		2
p-Hydroxy Phenyl, 3-Pyruvic Acid		1	1	2	3	2
p-Hydroxy Phenyl, 3-Propionic Acid			1	3		
Pyrogallol	2	1		1	2	2
Gallic Acid				1	1	1
Vanillin	2	3	3	12	5	6
Vanillic Alcohol				2	1	
Vanillic Acid	2	2	1	5	5	3
Acetovanillone	1			4	1	1
Ferulic Acid	1	1	1	4	3	7
Caffeic Acid	1		1	6	4	6
3-Methoxy, 4-Hydroxy Phenyl, 3-Pyruvic Alcohol		2	1	3	2	4
3-Methoxy, 4-Hydroxy Phenyl, 3-Pyruvic Acid		1	2	3		4
3-Methoxy, 4-Hydroxy Phenyl, 3-Propion- Aldehyde		1		2	2	3

TABLE 2b (Cont'd)

Compound	Direct Humic Acid		Humic Acid from Oxidized Coals				
	2	3	Lignites	Lignites	15		
					Rocky Mountain Province Coals	Interior Province Coals	Eastern Province Coals
3-Methoxy, 4-Hydroxy Phenyl, 3-Propanol							
3-Methoxy, 4-Hydroxy Phenyl, 3-Glyceric Acid	1	1	1	1	3	1	
Dehydrovanillone					2	1	
Syringic Aldehyde	1	1	1	1	5	3	2
Syringic Alcohol					3	2	4
Syringic Acid	2	1	1	1	7	5	3
3, 5-Dimethoxy, 4-Hydroxy Phenyl, 3-Pyruvic Aldehyde		2		1		1	4
3, 5-Dimethoxy, 4-Hydroxy Phenyl, 3-Propionic Acid					1		
3, 5-Dimethoxy, 4-Hydroxy Phenyl 3-Glyceric Acid						1	
3, 5-Dimethoxy, 4-Hydroxy Phenyl 3-Pyruvic Acid	1	1			2		
3, 5-Dimethoxy, 4-Hydroxy Cinnamic Acid					3	5	3
x, y-Dimethoxy Cinnamic Alcohol						1	
x, y-Dihydroxy Cinnamic Aldehyde						3	2

TABLE 3

Complex Phenols Identified of Unknown or Uncertain Biological Associations

Compound	Direct Humic Acid					Humic Acid from Oxidized Coals				
	2		3		Lignites	15		10		Eastern Province Coals
	Peats	Lignites	2	3		Rocky Province Coals	Interior Province Coals	10	Eastern Province Coals	
2,6-Xylenol			2		2	9	4		5	
3,5-Dihydroxy Toluene			1		1	1	1		1	
Hydroquinone	1	1								
x,y-Dimethoxy Phenol		1					2		1	
x-Phenyl Phenol							2		1	
x,y-Dihydroxy Benzophenone		2			1					
x-Methoxy Phenyl,										
3-Propionic Acid						6	1		1	
x-Methyl Benzoic Acid						1			1	
x-Methoxy Benzoic Acid						1	1		1	
2,5-Dihydroxy Benzoic Acid						2	2		3	
x,y-Dimethoxy Phenyl,										
3-Propionic Acid						1				
x,y-Dimethoxy Cinnamic										
Alcohol										
x,y-Dihydroxy, Monomethyl							1			
Benzoic Acid										
v,x-Dimethoxy, Y,Z-							3		1	
Dihydroxy Benzoic Acid						2				
v,x-Dimethyl, Y,Z-							1			
Dihydroxy Benzoic Acid						2	1			
1,2,4-Trihydroxy										
Benzoic Acid	2			2						
Saligerum						3				